

Performance characteristics of a pilot-scale biomass gasifier using oxygen-enriched air and steam

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HIGHLIGHTS

- ▶ This is a rare study of using a combination of “oxygen-enriched air” and steam as the gasifying agent for a 5 tons/day, pilot-scale biomass gasifier.
- ▶ Detailed measurements of syngas composition are conducted.
- ▶ Hydrogen and carbon monoxide concentrations in syngas can be increased by 70% and 34%, respectively, for particular feedstock.
- ▶ Oxygen-and-steam gasification is most effective for feedstock with low nitrogen and moisture contents.
- ▶ Ammonia and NOx concentrations in syngas increase as oxygen enrichment increases.

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ABSTRACT

This study is to investigate the characteristics of a biomass gasification system using mixtures of “oxygen-enriched air” and steam as the gasifying agent for increasing the syngas heating value and combustible gas constituents. This study also aims to characterize the effects of oxygen-and-steam gasification on ammonia concentration that can lead to significant NOx emissions from syngas combustion. Experiments are conducted using a pilot-scale, pressurized bubbling fluidized bed gasifier with a capacity of five tons per day. Pure oxygen is added to air before mixing with steam for gasification. A significant amount of steam is required to control the reactivity of the system at high oxygen levels. The oxygen content in the enriched air varies from 21, 45, to 80 vol.% on dry basis, corresponding to 21, 30, and 40 vol.% on wet basis respectively. The bed temperature is maintained at 800 °C for all tests. Three different biomass feedstocks with nitrogen contents varying from 0.05 to 1.4 wt.% are used for study (i.e., pine, maple-oak mixture, and discarded seed corn). The syngas dry composition is measured using a microgas chromatograph while ammonia concentration and moisture content are measured using a modified IEA Tar Protocol and Karl Fischer Titration respectively. Results indicate that oxygen-enriched air and steam gasification favors the production of combustible gas components including hydrogen, carbon monoxide, methane, and lighter hydrocarbons. When 40% oxygen is used, hydrogen increases by 70%, 47%, and 32% for pine, maple-oak, and seed corn respectively, while CO increases by 34%, 18%, and 8.6% respectively. Overall, it is found that oxygen and steam gasification is most effective for feedstock with low nitrogen and moisture contents. Results also show that ammonia and NOx concentrations in syngas increase as oxygen enrichment increases. The lower heating value of syngas can increase by as much as 43% for the feedstock studied. When the oxygen level increases from 21% to 40%, the H₂/CO ratio also increases from 0.59 to 0.75, 0.67 to 0.84, and 0.36 to 0.43 for pine, maple-oak, and seed corn respectively. Despite the improvement, the H₂/CO ratio is still moderate. The moderate H₂/CO ratio is explained by the high water content in syngas at high oxygen and steam conditions, indicating a large amount of un-reacted steam at the current gasifier temperature at 800 °C.

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1. Introduction

Recently there has been a renewed interest in using biomass as an energy source due to the increasing demand in global energy

coupled with environmental concerns of using fossil fuels. The pressure from stringent regulations on air pollution and greenhouse gas (GHG) emissions also makes biomass attractive since the use of biomass can reduce the life-cycle carbon emissions [1]. The conversion of biomass to biofuels can be achieved primarily via biochemical and thermochemical processes [2]. Many biochemical technologies are well developed and widely used for

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large-scale biofuel production such as corn ethanol and soy biodiesel. However, the production of corn ethanol and soy biodiesel from fermentation and transesterification processes, respectively, are only feasible with food crops as the feedstock. On the other hand, thermochemical processes can convert both food and non-food biomass to fuel products via gasification and pyrolysis. Among these methods, gasification is a more mature technology and is more widely used today [3].

Thermochemical gasification is a promising technology that can exploit the embedded energy in various types of biomass and convert to valuable products suitable for different industrial applications. Common feedstock for gasification includes agricultural crop residues, forest residues, energy crops, organic municipal wastes, and animal waste. Gasification takes place at moderately high temperature and turns solid biomass into combustible gas mixtures (known as synthesis gas or syngas) through simultaneous occurrence of exothermic oxidation and endothermic pyrolysis under limited oxygen supply [3–5]. The resulting syngas can be burned to produce heat or synthesized to produce liquid transportation fuels [1,2]. There are many factors that can affect the performance of biomass gasification, and the following review is focused on the effects of the gasifying agent.

The use of air as a gasifying agent is most common in industry but yields low heating value gas ($4\text{--}7\text{ MJ/Nm}^3$) that is only suitable for heat and power applications [6]. On the other hand, steam and oxygen can increase the heating value of syngas ($10\text{--}18\text{ MJ/Nm}^3$) and the H_2/CO ratio [3–6]. A high H_2/CO ratio is required for producing liquid fuels through Fischer–Tropsch synthesis and also benefits the production of H_2 for use in fuel cells. However, high capital costs and complex system design have hindered the applications of steam and oxygen gasification at a large industrial scale [7]. Therefore, studies were conducted using combinations of air, steam, and oxygen as the gasifying agent. For instance, the use of air–steam and oxygen–steam gasification can offer high gasification efficiency and high gas heating value without the need for a complex recirculation system (to provide heat for the endothermic steam gasification process) and high capital costs (for pure oxygen) [8–10].

Biomass gasification experiments using air and steam were conducted to investigate the effects of equivalence ratio, reactor temperature, and steam-to-biomass ratio on gasification performance [8]. It was found that adequate addition of steam can improve gas quality compared to air-only gasification. However, too much steam can decrease the gasification temperature, thus affecting the gas quality. A simulation study was conducted to understanding the effects of air–steam, oxygen-enriched air gasification [11]. It was reported that as the steam-to-air ratio increases, H_2 concentration increases whereas CO concentration and reaction temperature decrease, resulting in decreased gas heating value. On the

other hand, oxygen-enrichment shows increases in the concentrations of CO, CO_2 , H_2O , and H_2 .

Other experiments were also conducted using air, pure steam, and oxygen–steam mixture as the gasifying agent [6]. It was concluded that within the similar bed temperature range, both steam and oxygen–steam as the gasifying agent can yield higher gas heating values and higher H_2/CO ratios compared to air gasification. It was also found that steam gasification results in higher H_2 concentration but lower CO concentration in comparison to oxygen–steam gasification.

On the other hand, it was shown that oxygen-enriched air mixing with steam is also a very attractive gasifying agent for biomass gasification [12]. The oxygen levels were enriched up to 40 vol.% (dry basis). Results show that the gasification efficiency was improved from 54% to 68% and the lower heating value of the syngas increased from 5 to 9.3 MJ/Nm^3 when the oxygen level in the gasifying agent varied from 21 vol.% to 40 vol.% on dry basis. Another experimental study also shows that oxygen-enriched-air and steam gasification improves gas heating values; however, the peak temperature decreases due to the addition of steam [13]. It is also found that for both air-only and enriched-air gasification, the gas heating value decreases at richer conditions.

Despite the potential of air–steam–oxygen gasification, only limited literature is available as summarized in Table 1. Furthermore, the available literature is only focused on increasing H_2 , CO, CH_4 , and the gas heating value but neglects the effects on the formation of contaminants such as ammonia (NH_3). It is known that during gasification, nitrogen in biomass will be converted into nitrogen-containing compounds such as NH_3 and hydrogen cyanide (HCN) [17]. These nitrogen-containing compounds will release fuel-bound nitrogen (FBN) and leads to high NO_x emissions during combustion. High NO_x emissions can compromise the benefits of using biomass as a clean energy source. Hence it is crucial to characterize both the gas heating value and detailed syngas composition for biomass gasification using various gasifying agents.

The purpose of this study is to characterize the effects of mixtures of oxygen-enriched air and steam as the gasifying agent on the composition of syngas including the main constituents as well as the trace contaminant of ammonia, the main nitrogen-containing compound.

2. Experimental setup

2.1. Feedstock

The biomass feedstock used include pine, maple and oak mixture (50/50 by weight), and discarded seed corn. Pine and maple-oak mixture are in pellet form. The pellets are cylindrically shaped

Table 1
Summary of literature specifically on air–oxygen–steam biomass gasification.

Ref.	Gasifying agent			Reactor T (°C)	Gasifier type	Feedstock	Main gas components analyzed	NH_3 analyzed
	Air	Oxygen	Steam					
Gil et al. [6]		X	X	780–890	Fluidized bed	Pine wood	H_2 , CO, CH_4 , CO_2	No
Lv et al. [8]	X		X	700–900	Fluidized bed	Pine sawdust	H_2 , CO, CH_4 , CO_2 , C_2H_2 , C_2H_4 , C_2H_6	No
Lv et al. [9]		X	X	774–934	Downdraft	Pine wood	H_2 , CO, CH_4 , CO_2 , C_2H_4 , C_2H_6	No
Campoy et al. [12]	X	X	X	755–840	Fluidized bed	Wood pellet	H_2 , CO, CH_4 , CO_2	No
Thanapal et al. [13]	X	X	X	Varied	Fixed bed	Dairy biomass	H_2 , CO, CH_4 , CO_2	No
Zhou et al. [14]		X		1000–1400	Entrained-flow	Rice husk; sawdust; camphor wood	H_2 , CO, CH_4 , CO_2	No
Umeki et al. [15]			X	427–627	Updraft	Wood chip	H_2 , CO, CH_4 , CO_2	No
Wei et al. [16]			X	750–850	Free-fall reactor	Legume straw; pine sawdust	H_2 , CO, CH_4 , CO_2 , C_2H_2 , C_2H_4 , C_2H_6	No

Table 2
Feedstock ultimate and proximate analyses.

Feedstock	Wood (pine)	Wood (oak + maple)	Seed corn	
Proximate analysis (wt.%)				
Volatiles	74	75.11	66.43	±1.0
Fixed Carbon	16.66	16.81	17.15	±1.0
Moisture	8.9	6.25	15.01	±0.1
Ash	0.43	1.83	1.4	±0.1
Ultimate analysis (wt.%)				
C	47.52	46.56	40.07	±0.3
H	6.5	6.24	7.1	±0.3
N	0.05	0.14	1.4	±0.2
O	46.36	46.13	50.5	±0.5
S	0.01	0.02	0.17	±0.05

with 0.25 inches in diameter and 0.5 inches in length. According to the ultimate analysis, the overall molecular formulas are $C_nH_{1.63n}O_{0.73n}$, $C_nH_{1.6n}O_{0.74n}$, and $C_nH_{2.11n}O_{0.95n}$ for pine, maple-oak, and seed corn, respectively. Proximate and ultimate analyses of all the feedstock are reported in Table 2. These data are reported on “as received” basis. The analyses only report the main elemental species, CHONS, without other trace species such as chloride and minerals.

Ammonia concentration in syngas depends on the nitrogen content of the feedstock, operating conditions, and gasifying agents used [18–20]. Nitrogen in the feedstock is the primary factor affecting ammonia concentration in syngas. During syngas combustion, ammonia oxidation can lead to significant NOx emissions.

Therefore, it is of critical interest to study the effects of feedstock on ammonia concentration when oxygen-enriched air and steam is used as the gasifying agent. The three feedstocks, with low to high nitrogen contents, can allow one to study this effect.

2.2. Gasification system

A pilot-scale pressurized bubbling fluidized bed gasifier is used in this study. The gasifier has the capability to operate up to 50 psig and can use pure air or oxygen-enriched air in combination with steam as the gasifying agent. The gasification system is rated at approximately 800 kW, corresponding to 180 kg/hr of raw biomass with an average heating value of 16 MJ/kg. The gasifier is operated based on the autothermal concept, i.e., part of the feedstock is used to provide heat for the gasification process. A schematic diagram of the overall gasification and sampling systems is shown in Fig. 1. The gasification system consists of a biomass feeding system, liquid oxygen system, steam generation unit, fluidized bed reactor, and gas cleanup components that include a baghouse filter and a cyclone.

The feeding system has three components, including a feeding hopper and two pressurized vessels. Pelletized feedstock are first loaded into the feeding hopper and then transported to a vessel at atmospheric pressure using a feed auger. The feeding auger is screw-operated that feeds the biomass into the vessel at a constant rate. The diameter of the screw feeder limits the maximum size of the feedstock to one inch in diameter. Once the first vessel is full, it is pressurized to 15–18 psig (approximately 2 bar) and biomass is

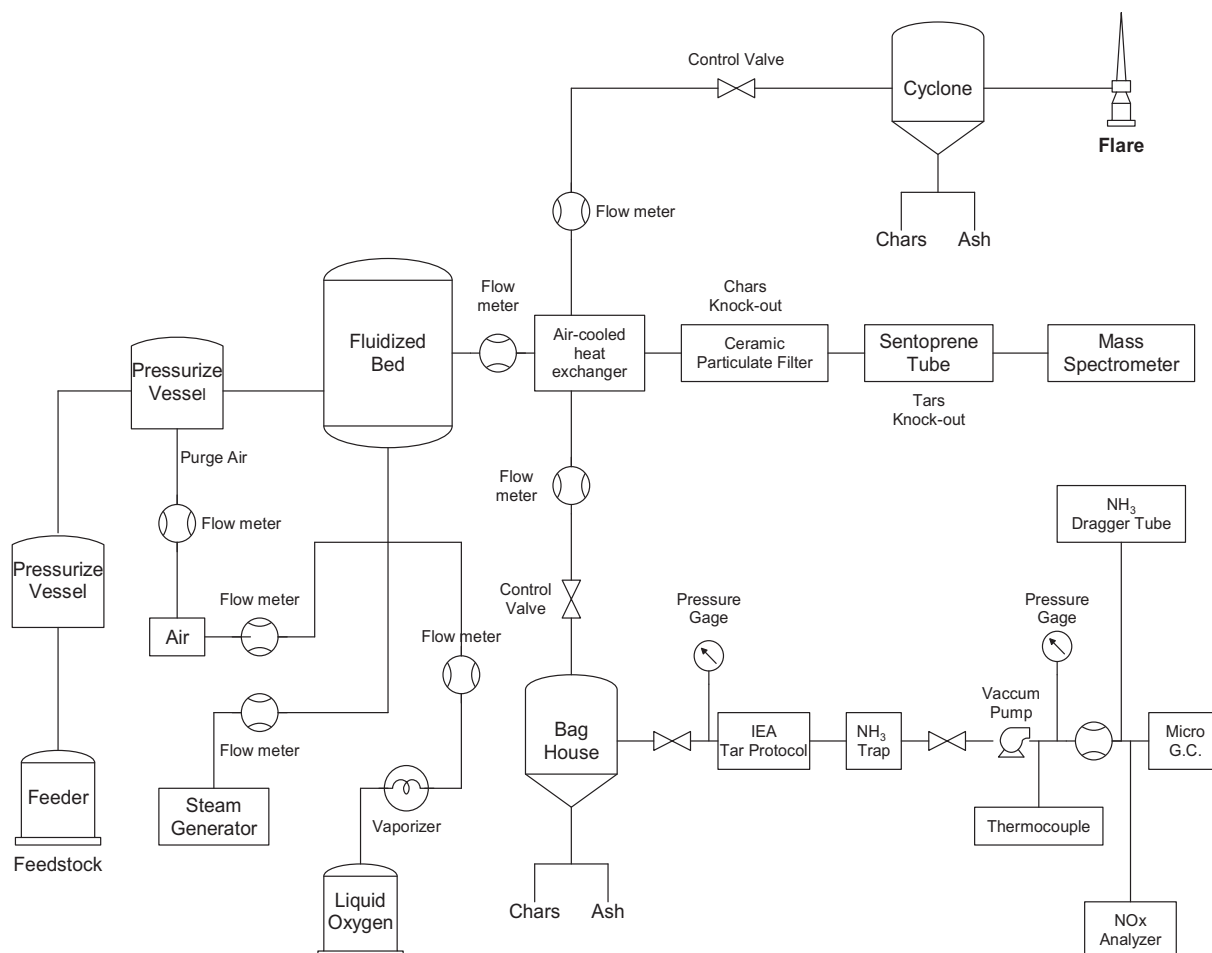


Fig. 1. Schematic of the present gasification and sampling systems.

transferred to another pressurized vessel via the same pressure and feeding mechanism. Finally, biomass is introduced into the fluidized bed reactor. During gasification, air is purged into the second pressurized vessel in order to prevent the backflow of combustible syngas from the reactor to prevent explosion.

The oxygen system comprises of a 1500-gallon liquid oxygen tank. The system is designed for operation duration of 72 h at 2500 SCFH maximum flow of pure oxygen gas to produce blends of oxygen and air up to 90% oxygen purity. Liquid oxygen in the tank is maintained at -400°F (-204°C), and safety barriers such as fences and bollards are built surrounding the tank. During the operation, liquid oxygen passes through a vaporizer at 250 psig (18.3 bar) and is converted to gas phase. The pure oxygen gas then passes through a gas flow meter at 100 psig (7.9 bar) at room temperature to mix with air and steam before entering the fluidized bed reactor.

Before each test, the gasifier is warmed up overnight with pre-heated air (using electric circulating air heater) at approximately 538°C . Next, a small flow (40 lbs per hour, PPH) of biomass is fed into the gasifier and the system is operated in combustion mode for several hours. During this time the reactor is operated at about $840\text{--}870^{\circ}\text{C}$ in combustion mode while all the downstream equipment is warmed up to at least 316°C to prevent tar condensation (on pipes between the baghouse filter, cyclone, and fluidized bed reactor) when switched to gasification mode. When all the desired temperature are established, biomass feed rate is increased to reduce air to fuel ratio for transition from combustion to gasification. After air gasification mode is established, the transition to oxygen-enriched mode begins. This operation usually takes 10–15 min to reach steady-state conditions, i.e., stable system temperature. The transition is a simultaneous reduction of air flow and an increase of oxygen and steam flows to achieve the desired level of oxygen operation. Steam is generated using a boiler using natural gas. The stream of air–oxygen–steam fluidizing agent is well mixed before entering the reactor as a single fluid stream. Control systems are established for air, oxygen, and steam in order to monitor, record, and control the desired flow rate.

The fluidized bed temperature is continuously monitored using four K-type thermocouples. The bed temperature for all the tests is kept at approximately 800°C . The bed temperature is kept constant by adjusting the steam flow rate to modulate the reactivity when more oxygen is used. As seen in Table 3, the steam to oxygen ratio (S/O) is increased as more oxygen is used. The fluidized bed has a bed depth of 1–1.3 m and is operated under pressure varying between 10 and 20 psig (1.7–2.4 bar). The inner wall of the fluidized bed reactor is surrounded by refractory lining to minimize heat loss. At the bottom of the reactor, there are always silica sand and limestone present. Silica sand is used as a fluidizing medium whereas limestone is used to prevent bed agglomeration and reduce tar formation.

2.3. Gas sampling system and procedures

Sampling and analyses of syngas are carried out using two different methods, continuous online sampling and off-line wet-chemical approach. The sampling locations are also shown in Fig. 1. The continuous online sampling is carried out using various analyzers. Dry gas compositions are analyzed using microgas chromatograph (micro GC) manufactured by Varian Inc., Model CP-4900. The micro GC is equipped with four different columns capable of measuring CO, CO₂, H₂, N₂, O₂, CH₄, C₂H₂, C₂H₄, C₂H₆ and C₃H₈ with the sampling interval set at 120 s. NO_x in syngas is measured using a NO_x analyzer utilizing chemical cells. These gas analyzers display real-time data to help monitor the system operation. It is worth noting that originally a mass spectrometer is used but it is not able to provide reliable measurements due to two reasons. First, the mass spectrometer detects and differentiates gas species by atomic mass unit (amu). Ammonia and water have amu of 17 and 18, respectively, making it difficult to distinguish. Second, as syngas is cooled from 400°C to 80°C , ammonia tends to react with HCl to form solid ammonium chloride (NH₄Cl). As a result, the non-negligible formation of NH₄Cl further contributes to the uncertainty of ammonia measurement using mass spectrometer. Therefore, an off-line, wet-chemical approach is used for ammonia measurement based on the modified IEA (International Energy Agency) Tar Protocol [21].

In this study, IEA Tar Protocol is implemented to simultaneously capture ammonia, tars, and moisture in syngas. The IEA protocol is based on the principle of discontinuous sampling of a gas stream containing particles and tars under iso-kinetic conditions. Hot syngas exits the fluidized bed reactor at 800°C and goes through a gas cleaning stage (baghouse) to knock out solid residues such as chars and ash before sampling for gas composition analysis. The gas exits the baghouse at 400°C and enters the impinge train as shown in Fig. 2. This setup aims for collecting tars and condensing water vapor out of the syngas. This setup consists of a set of six impingers placed in temperature controlled baths.

These impingers contain isopropyl alcohol (IPA) solvents to absorb tars. The first impinger contained 100 mL of IPA while impingers 2–5 are filled with 50 mL of IPA and the sixth impinger is left empty for capturing aerosols. Some of the impingers are placed in a hot bath at 40°C (impingers 1, 2, 4) and some are placed in a cold bath between -20°C and -15°C (impingers 3, 5, 6) using mixtures of ice, water, and salts. A closed-loop heating system is used to keep the hot bath temperature constant while the cold bath temperature is monitored and maintained manually during each test run. The hot and cold baths create two different temperature gradients that enable the hot sample gas to gradually cool down in two steps. As sample gas enters impinger 1, large quantities of tars and moisture are absorbed by the vaporized IPA solvent and then condensed (boiling point of tar is 80°C). Subsequently, all tars and moisture will drop out from sample gas as they passed through

Table 3
Operating conditions.

Feedstock	Pine			Maple-oak			Seed corn		
	21	30	40	21	30	40	21	30	40
Oxygen percent (wet basis)	21	30	40	21	30	40	21	30	40
Bed temperature ($^{\circ}\text{C}$)	800	800	800	800	800	800	800	800	800
Biomass (lb/hr)	190	290	350	250	345	370	190	290	375
Air (lb/hr)	202	94	29	275	117	31	202	94	32
Steam (lb/hr)	0	49	59	0	52	67	0	49	65
Oxygen (lb/hr)	0	48	73	0	51	82	0	48	81
ER	0.19	0.29	0.29	0.20	0.28	0.31	0.22	0.34	0.34
S/B	0	0.17	0.17	0	0.15	0.18	0	0.17	0.17
S/O	0	0.70	0.74	0	0.67	0.75	0	0.70	0.74
O/B	0.25	0.39	0.38	0.25	0.36	0.40	0.25	0.39	0.39
(H ₂ O + O ₂)/B	0	0.41	0.40	0	0.38	0.42	0	0.41	0.41

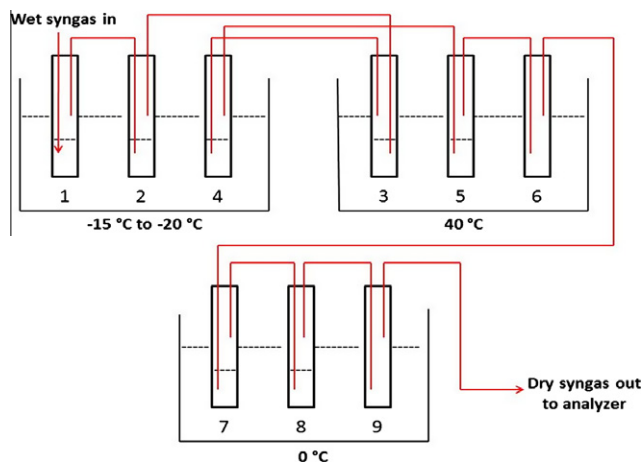


Fig. 2. Setup of impingers based on modified IEA Tar Protocol.

the remaining impingers. Ammonia gas and solid ammonium chloride also drop out of the syngas stream and are collected in the impingers.

The IEA Tar Protocol guideline is originally developed for tar quantification. In order to ensure efficient ammonia capturing, a second set of three impingers downstream of the first set is added to prevent ammonia slip. All three impingers are immersed in cold bath maintained at 0 °C with the first two filled with 150 mL of HPLC (high performance liquid chromatography) grade water. The amount of ammonia slip through impingers 1–6 depends on the amount of moisture in the syngas, i.e., the lower the moisture, the more ammonia will slip through. This is because ammonia is condensed with water, thus when the moisture in the syngas is low, there is not enough water for ammonia containment. In order to check if the combination of two impinger sets is able to completely capture ammonia, Ammonia Dräger tubes are also used to check the ammonia slip after the second impinger set. Ammonia Dräger tubes are used at numerous times during experiments and no detection of ammonia slip is found.

According to the IEA Tar Protocol, a minimum of 7 and maximum of 10 ft³ of gas should be flown through the impinger sets. The volumetric flow rate of the sample gas is measured and recorded using a calibrated dry gas meter. After reaching the desired gas flow, the sampling valve is closed and the impingers are allowed to cool down for 15–20 min to reduce the pressure within the impingers. This is very important because the sample will flow out of impingers if impingers are detached from sampling lines immediately after the sample line is shut off, resulting in loss of sample gas.

The sample in impingers is then transferred into separate high density polyethylene (HDPE) bottles. Samples from the first six impingers are collected into two bottles named primary and rinse. The primary bottle is used to collect samples directly out of the hot and cold bath impingers whereas the rinse bottle contains mixture of solvents and sample residues from impingers and impingers' connections. Solvents such as IPA, dichloromethane (DCM), and methanol are used to dissolve tars, and water is used to collect salts within impingers and connection tubes. This is to ensure that all samples are collected. Since syngas gives off very strong odors, collection of samples from impingers needs to take place under a fume hood.

The HDPE bottles are tightly sealed and stored at less than 5 °C for later analysis. The sample from the second set only consists of ammonia and water mixture, therefore can be directly analyzed for ammonia concentration. This sample is stored in bottles labeled 7, 8 and 9. Ideally, all samples should be analyzed within one week because ammonia will evaporate and escape over time.

2.4. Sample analysis

Since the sample from the first six impingers contains mixture of tars, water, solvents, solid ammonium chloride, and very small amount of chars, intermediate steps are required for separating heavy tar substances from the rest.

Analyses of ammonia in the sample collected from the first impinger set are conducted in three primary steps. First, char particles in primary and rinse bottles are filtered before going through a roto-evaporating process to evaporate solvents and salts dissolved in water mixtures. As a result, only tars are retained and are quantified gravimetrically. Filtration is performed using Whatman No. 42 filters in a Buchner funnel coupled to an Erlenmeyer flask with a sidearm where a vacuum pump is attached to speed up the filtering process. To prevent ammonia from escaping in gas phase, the other end of the pump is connected to a set of three impingers (labeled 10, 11, 12) in the ice bath containing HPLC grade water. The filter paper is then thoroughly rinsed with water and solvents (IPA and DCM) to ensure that no ammonium salts and tars are retained by the filter paper.

Roto-evaporating is a process similar to distillation that allows for the separation of liquids of different chemical compounds according to their boiling points. The equipment consists of a roto-evaporating unit, a chiller, and a pump. The roto-evaporating unit consists of six temperature treated glasses that hold evenly distributed amount of samples from primary and rinse bottles. This unit is connected to both the pump and the chiller unit. The pump is used to create a vacuum condition within the unit and the chiller contains a glass bottle to capture the evaporated samples. The temperature of the chiller is set at –105 °C in order to prevent ammonia from vaporizing and escaping in gas phase.

The overall roto-evaporating process takes place at a maximum temperature of 55 °C to prevent tars from boiling and mixing with solvents and salt water. The six sample glasses are subject to revolving motion throughout the evaporating process so that uniform temperature can be achieved. The process can take up to between 4 and 8 h depending on how much water is used during rinsing. After the process is completed, meaning only dry tars on the bottom of the glasses, the sample collected from chiller is poured into another HDPE bottle labeled “distillated.” The weights of all six glasses before and after the process are recorded to quantify tar concentration.

The second step involves using Aquanal ammonium test kits containing three reagents to shift the pH value of the roto-vap solution to convert free ammonia in sample to ammonium ions. Ammonium ions are then reacted with hypochlorite and thymol to cause color change of solution (green). The intensity of green color is directly proportional to ammonia concentration in the sample.

The third step is to pass the color-changed solution to an Ultra-violet–Visible spectrophotometer (UV–Vis). The UV–Vis measures the energy of light before entering and after leaving the sample. The difference is the amount of absorbed energy and is directly proportional to the ammonia concentration in the sample. Ammonia concentration in syngas is then calculated by using the known ammonia concentration in analyzed samples and the measured gas volume flow during the sampling time interval.

Biomass-derived gas contains certain amount of water vapor which heavily depends on the feedstock and operation conditions. Determining water content in syngas is very important since it directly affect gas heating value, flame speed, and flammability limits. Karl Fischer Titration method is used to determine water content from collected sample in impingers. This method determines water content in the substance by measuring the electricity needed for electrolysis process to produce iodine amount to completely react with water in the substance. Right before roto-evaporating pro-

cess, small quantity (around 1 mL) from the primary bottle after filtered is saved for water tests – only the primary sample is used because of not being diluted by solvents. For every sample, three water tests are run and the averaged value is reported. This water content is then used to convert dry gas composition measured by micro GC to wet gas basis – the actual syngas composition, which is necessary for determining the amount of air needed at different combustion equivalence ratios in the burner.

3. Results

3.1. Operating conditions

Tests are conducted for three different biomass feedstocks with each feedstock at three different oxygen concentrations in the gasifying agent. Therefore, nine different sets of syngas compositions are obtained. Since the objective of this study is to investigate the effects of oxygen-enriched air and steam on syngas composition at a fixed bed temperature of 800 °C, no significant variations in the equivalence ratio are intended when the oxygen level changes from 21% to 40% on wet basis. The equivalence ratio (ER) is defined as the ratio of actual air–fuel ratio to the stoichiometric air–fuel ratio, i.e., ER less than 1 for rich conditions [3]. This definition of equivalence ratio is commonly used in the gasification industry and it is opposite to that used in combustion applications. In this study, the ER range for pine wood, maple-oak wood, and seed corn are 0.19–0.29, 0.20–0.31, and 0.22–0.34 respectively. Table 3 provides the flow rates for air, steam, oxygen, and biomass feedstock at different operating conditions. Table 3 also includes data on fluidized bed temperature, ER, steam-to-biomass ratio (S/B), oxygen-to-biomass ratio (O/B), steam-to-oxygen ratio (S/O), and steam-and-oxygen to biomass ratio, (S + O)/B. The O/B ratio is the mass ratio of the total oxygen fed to the reactor to biomass, in which total oxygen includes pure oxygen, oxygen from air, and oxygen from steam. This total oxygen is also used for calculating ER.

3.2. Syngas composition

The dry composition of syngas (except ammonia and tars) is measured using a micro GC. The measurement uncertainty is $\pm 5\%$ according to the equipment specifications. During the measurement, the gas composition reading is very stable with a maximum fluctuation of 3% for N₂ and 2% for all other gas species. For each feedstock, two separate tests are run and the averaged results are

showed in Table 4. Results from two test runs are within 2% difference. Table 4 also summarizes the tar content, ammonia concentration, gas composition (wet basis), lower heating value (LHV), and adiabatic flame temperature of the syngas derived from each feedstock at different oxygen levels. The gas composition is reported on wet basis. Reporting gas composition on wet basis, as in this study, is more difficult but more practical because the wet composition represents the real composition. It is well known that biomass has high moisture levels that can affect syngas quality. Thus, wet composition is a better indicator of the syngas quality for end application. Notice that some data are not obtained due to loss of information and equipment malfunction on the test days. Due to the complexity of operating the present pilot-scale gasifier, additional tests are not conducted later on.

From Table 4, one can see that all the main gas constituents have similar increasing trends for all biomass feedstock when oxygen concentration increases from 21 to 40 vol.%. Therefore, results of one feedstock will be chosen for discussion (pine wood) but the performance comparison among different biomass feedstock will also be included.

4. Discussions

4.1. Hydrogen content

Figs. 3–5 show that the hydrogen content increases as oxygen concentration increases from 21 to 40 vol.%. The hydrogen content in syngas for pine wood increases from 9.47 to 16.09 vol.%, approximately 70% improvement. Literature indicates that temperature is also an important parameter for increasing hydrogen content of syngas [8,14]. Increasing temperature will favor the forward reaction of the steam reforming reaction and convert methane and water into CO and H₂. Moreover, higher temperature can enhance the forward rate of the water–gas reaction to convert solid carbon (in chars) to CO and H₂. High temperature also favors the production of CO in the Boudouard reaction, which in turn can increase H₂ production via the water–gas shift reaction. However, since the bed temperature is kept constant throughout the tests, the increase in H₂ must be from other factors such as steam.

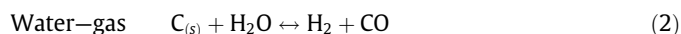
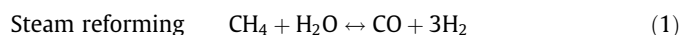


Table 4
Syngas composition (wet basis).

Feedstock	Pine wood			Maple-oak wood			Seed corn		
	21% O ₂ (%v/v)	30% O ₂ (%v/v)	40% O ₂ (%v/v)	21% O ₂ (%v/v)	30% O ₂ (%v/v)	40% O ₂ (%v/v)	21% O ₂ (%v/v)	30% O ₂ (%v/v)	40% O ₂ (%v/v)
H ₂	9.47	14.92	16.09	11.33	15.04	16.65	4.43	5.46	5.86
CO	16.09	19.23	21.50	16.91	18.40	19.93	12.42	13.09	13.49
CO ₂	13.09	18.03	19.51	13.56	17.92	19.68	10.91	12.17	12.74
N ₂	38.03	15.06	5.76	39.02	17.80	5.20	41.60	15.36	5.02
NH ₃	0.02	0.02	0.02	0.06	0.09	0.11	0.53	0.68	0.89
NO _x	0.01	0.02	0.03	X	X	X	0.03	0.05	0.04
H ₂ O	13.05	24.35	29.75	9.97	21.94	27.34	21.65	44.56	55.85
CH ₄	5.50	6.29	7.10	5.27	6.38	6.82	3.59	4.14	4.24
C ₂ H ₂	0.09	0.10	0.12	0.07	0.08	0.10	0.16	0.15	0.14
C ₂ H ₄	1.56	1.67	1.99	1.18	1.48	1.70	1.76	1.88	1.97
C ₂ H ₆	0.39	0.38	0.46	0.26	0.43	0.42	0.27	0.31	0.32
C ₃ H ₈	0.21	0.21	0.30	0.07	0.19	0.17	0.20	0.27	0.24
Tars (g/m ³)	13.78	18.67	19.55	X	8.18	6.62	13.47	X	11.39
LHV (MJ/kg)	5.77	7.27	8.26	5.58	7.11	8.09	4.28	5.22	5.49
T _{ad} (K)	1929	2006	2050	1932	1999	2042	1744	1765	1755
Molecular mass (kg/kmol)	25.03	23.94	23.92	24.98	23.98	22.77	25.3	23.04	22.6

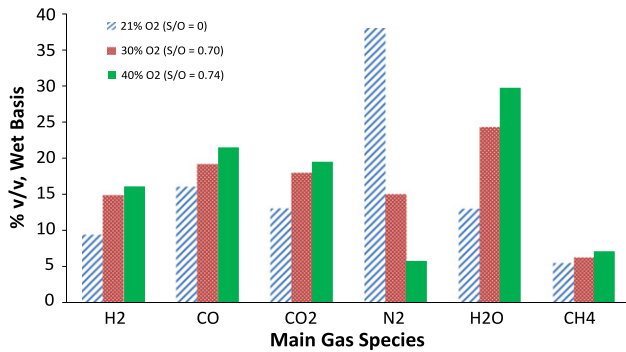


Fig. 3. Main gas compositions using pine wood.

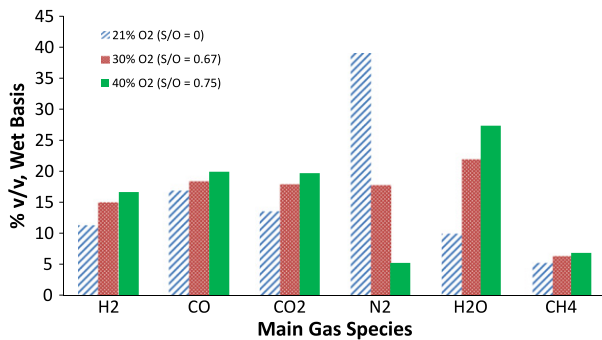


Fig. 4. Main gas compositions using maple-oak mixture.

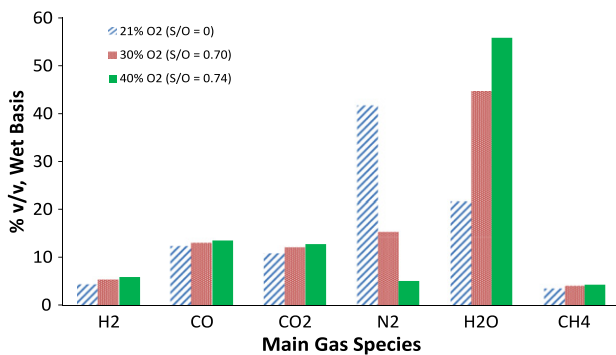
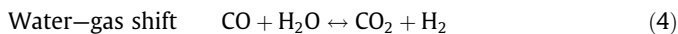


Fig. 5. Main gas compositions using seed corn.



In both the steam reforming and water-gas reactions, higher steam concentration will result in more H_2 when reactions reach equilibrium. Figs. 3–5 all show the same trend of increasing H_2 content in syngas as the S/O ratio increases. The S/O for 30 and 40 vol.% for pine wood are 0.70 and 0.74, respectively. This indicates that steam can be an important driving force for the increase in H_2 concentration in syngas. The increase in oxygen percentage alone may have adverse effects on hydrogen concentration due to oxidation reactions that possibly convert H_2 to H_2O . However, an appropriate level of oxygen is still needed since the presence of oxygen in the gasifying medium is very important to initiate the exothermic reactions that provide energy for the above endothermic reactions to produce more H_2 . Oxygen can also react with solid carbon to form CO at the gasification condition (i.e., fuel rich) which in turn undergoes water-gas shift to produce more H_2 . Nonetheless, the final syngas composition is a collective result of

the overall operating conditions under increased oxygen and steam levels. Thus, it is difficult to isolate the effect of individual gasifying agents.

According to previous studies [8,10], reactions Eqs. (1)–(3) are most favorable when gasification temperature is above 800°C because higher temperature provides more energy for the endothermic reaction of steam. This is evidenced from the high water content in syngas shown in Figs. 3–5. The increase in water content in syngas from 13% to 29% (going from 21 to 40 vol.% of oxygen level) indicates that a large fraction of steam are not effectively utilized at a fixed bed temperature of 800°C .

Ultimate analyses of the feedstock from Table 2 show that seed corn has the highest hydrogen content followed by maple-oak and pine wood. Thus, one would expect that hydrogen content in syngas would be highest for seed corn. However, results show that syngas produced from seed corn has the lowest hydrogen content. One possible explanation is that since the moisture content of seed corn is almost twice compared to pine wood and maple-oak wood, more energy from the oxidation reaction is utilized during the drying stage. Ultimately, less energy is left for driving the endothermic reactions of steam to produce H_2 and CO. The H_2 and CO contents in syngas for seed corn are only improved by 6.7% and 8.6% respectively, which are relatively low compared to the other two feedstocks.

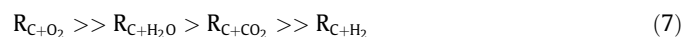
4.2. CO content

Similar to H_2 , CO content in syngas increases when oxygen percentage changes from 21 to 40 vol.%. However, the magnitude of the increase in CO is much less than H_2 . This is because three moles of H_2 are produced while only one mole of CO is produced according to the steam reforming reaction. Furthermore, high steam concentration will also result in high H_2 production at the expense of depleting CO, according to the water-gas shift reaction. When oxygen percentage in the gasifying medium increases from 21 to 40 vol.%, CO ranges from 16.1% to 21.5%, 16.9% to 19.9%, and 12.4% to 13.5% for pine, maple-oak, and seed corn respectively.

When more oxygen is introduced into the reactor, carbon conversion efficiency is increased because extra oxygen is available to enhance the oxidation reactions, thus releasing more heat to accelerate the gasification process. Most gasification processes do not reach true equilibrium due to the short residence time. Therefore, by accelerating the gasification process, there is a chance to further crack down more carbon within chars, resulting in an increase in the total carbon content in the syngas. Oxygen and steam are both possible candidates for reacting with chars to produce CO_2 , CO, and CH_4 as shown in Eqs. (2), (5), and (6).



Previous literature indicates that the carbon conversion rate is the fastest when pure oxygen is used as a gasifying agent [3]. Therefore, more CO will be produced in comparison to CH_4 due to the higher rate of char-C reacting with oxygen (Eq. (5)) than reacting with steam (Eq. (6)). The relative carbon conversion rate is as follows.



Again, CO will react with steam in the water-gas shift reaction to produce CO_2 and H_2 . Nonetheless, increasing oxygen in the gasifying agent does increase CO content in syngas, as also observed in the present study.

4.3. Effects of oxygen-to-biomass ratio on H_2/CO ratio

H_2 and CO are the most important gas components of syngas and can determine the syngas quality and downstream applications. For instance, to synthesize syngas into liquid fuels using Fischer–Tropsch processes, the optimal H_2/CO ratio is 2. In this study, although significant improvements in H_2 and CO are observed for all three feedstocks, the H_2/CO ratio is still below 2 under the current operating conditions. Nonetheless, Fig. 6 shows that there is a positive relationship between O_2 /biomass and H_2/CO ratios. Further experiments can be conducted to explore the extent of the increase in the H_2/CO ratio as more oxygen is used for gasification.

4.4. CO_2 content

The amount of CO_2 in syngas is between 13 and 20 vol.% for both wood feedstock, and between 11 and 13 vol.% for seed corn. Notice that when oxygen percentage increases to 30 and 40 vol.%, the difference between CO and CO_2 becomes smaller. The increase in CO_2 is expected because higher amount of O_2 will enhance CO conversion to CO_2 . Moreover, steam helps increase H_2 yield but at the expense of oxidizing CO to CO_2 . Since the amount of CO_2 does not increase in the same magnitude as the oxygen fed, this may imply that some CO_2 react with chars through Boudouard reaction to produce CO, thus limiting the final CO_2 output.

The limestone used in the gasifier can also contribute to the production of CO_2 . The effects of limestone calcination on CO_2 production vary in the literature [22,23]. In the present study, the limestone is not continually fed and the fluidized bed temperature is maintained at 800 °C, which is lower than that in a previous literature [23]. There is not a direct way to evaluate the contribution of CO_2 resulting from the limestone calcination. During the experiment, data are taken as soon as the system reaches steady state, thus the calcination of limestone may not be significant during the gas sampling. Furthermore, syngas is sampled continuously for 30–60 min and the CO_2 reading is relatively steady during the measurement.

4.5. Light hydrocarbon content

For all three biomass feedstocks, very little increase in CH_4 and other light hydrocarbons is observed. Pine wood has the highest increase at 1.58 vol.%, followed by maple-oak at 1.55 vol.%, and seed corn at 0.65 vol.% when oxygen percentage is increased from 21% to 40%. All C_2 species are below 0.5% except for ethylene (C_2H_4) which is between 1.2 and 2.0 vol.%. An improvement in CH_4 yield is achieved through methanation reactions due to more CO and H_2 .

4.6. Gas heating value

The syngas heating value is directly proportional to the concentration of combustible gas constituents such as H_2 , CO and CH_4 and is inversely proportional to water and nitrogen concentrations. As oxygen percentage increases from 21 to 40 vol.%, combustible gas constituents increase and nitrogen decreases, thus resulting in higher gas heating value. Results show that the lower heating value increases by 43%, 45%, and 28% for pine, maple-oak, and seed corn, respectively. The smaller improvement in the gas heating value derived from seed corn is due to the substantial moisture in syngas as shown in Table 4. This is because water does not contribute to the energy release but it absorbs energy from combustion, thus reducing the heating value per unit mass of the gas mixture.

4.7. Ammonia and NO_x contents

During gasification, nitrogen in biomass will be converted to nitrogen-containing species such as NH_3 , HCN, NO, char-N, tar-N, and N_2 . It has been shown that NH_3 concentration is the second highest (after N_2) among the nitrogen-containing species and its concentration in syngas increases as nitrogen content in the feedstock increases [19,24,25]. It is widely accepted that a majority of NH_3 in syngas are formed from volatile-N that are released during the pyrolysis stage. On the other hand, previous experiments show that a certain percentage of biomass nitrogen resides within tars and chars (0.7–9.4% in chars and 0.37–1.3% in tars) [25]. Thus, non-negligible amount of NH_3 can also result from thermal cracking reactions of tars and chars in the presence of steam and oxygen.

Steam in the gasifier can result in a large amount of hydrogen radicals that can react with radicals in solid char to enhance the breakdown and gradual hydrogenation of char-N into NH_3 [25]. Since the oxygen flow rate increases with steam flow rate in order to keep the bed temperature fixed at 800 °C, NH_3 concentration can also be correlated with oxygen percentage in the gasifying agent, as seen in Fig. 7 and Table 4. Among the three feedstocks studied, seed corn and maple-oak have significant increases in NH_3 concentration, approximately a 70% increase when oxygen percentage increases from 21 to 40 vol.%. On the other hand, for pine wood, NH_3 remains approximately the same for various oxygen percentages.

As mentioned earlier, thermal cracking of steam provides the source of hydrogen and hydroxide radicals (H and OH) that could react and form stable species such as H_2 . These radicals can also react with the nitrogen released from biomass during gasification to form NH_3 . Since pine has low nitrogen content, there will be less competition for hydrogen radicals and thus more H_2 can be produced in syngas. This is shown by results presented in Table 4. According to Table 4, pine has the highest H_2 improvement and lowest NH_3 concentration whereas seed corn has the lowest H_2

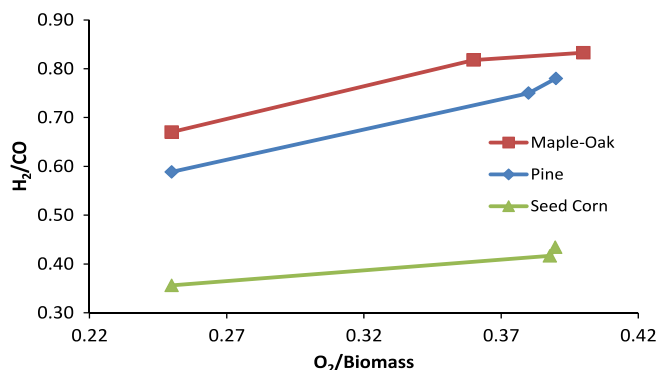


Fig. 6. Effects of oxygen/biomass ratio on H_2/CO ratio.

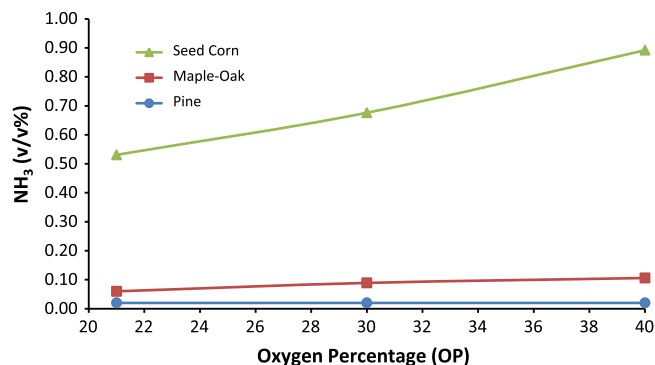


Fig. 7. Comparisons of NH_3 concentrations in syngas for different oxygen levels.

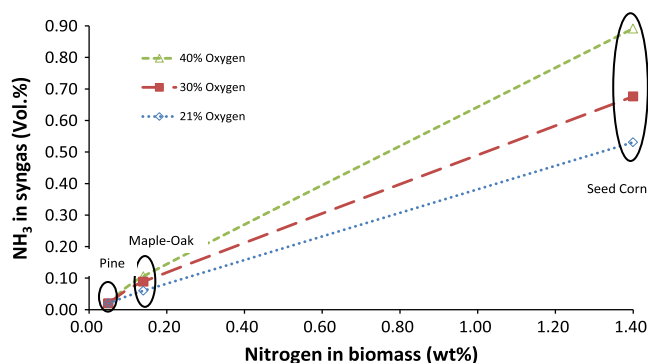


Fig. 8. Effects of nitrogen content in biomass (wt.%) on ammonia concentration (vol.%) in syngas at different oxygen enrichment conditions.

improvement and highest NH_3 concentration. Another evidence for hydrogen radicals competition is the level of N_2 in syngas. At 40 vol.% oxygen conditions, seed corn has the highest nitrogen content but N_2 concentration in syngas is the lowest, indicating that more volatile-N may react with hydrogen radicals to form more NH_3 rather than being converted to N_2 . On the other hand, pine has the lowest nitrogen content, thus the amount of volatile-N released is insignificant, which gives hydrogen radicals more opportunities to react to form H_2 . Overall, the experimental results indicate that oxygen-enriched air and steam gasification is more effective for biomass with low nitrogen content.

Fig. 7 shows the effects of increasing oxygen percentage in the gasifying medium on NH_3 concentration for all three feedstocks. It is found that NH_3 concentration in syngas for medium to high nitrogen content feedstocks (maple-oak and seed corn) is correlated with oxygen level in syngas. On the other hand, Fig. 8 shows the relationship between nitrogen in feedstock and NH_3 concentration in syngas. It can be seen that higher nitrogen in biomass will result in higher NH_3 concentration in syngas at the same oxygen level in the gasifying medium. Another observation is that the higher the nitrogen content in feedstock, the more sensitive it is in forming NH_3 at high oxygen levels.

Fig. 9 shows NO_x concentration in syngas for different oxygen levels in the gasifying medium. Note that NO_x concentrations are measured only for pine and seed corn due to technical difficulties during the allowable time for testing. In general, NO_x concentration in syngas increases as oxygen in the gasifying medium increases. Notice that for seed corn using 40 vol.% oxygen, NO_x concentration decreases slightly. In fact, seed corn results in a significant amount of moisture in syngas as oxygen in the gasifying medium increases. If the NO_x data are converted to dry basis,

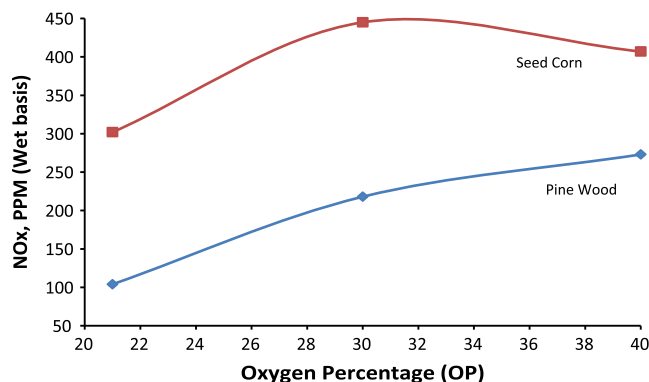


Fig. 9. Comparisons of NO_x (wet basis) in syngas for different oxygen levels.

NO_x in syngas also increases monotonically, i.e., 388, 813, and 941 ppm for 21, 30, and 40 vol.% oxygen levels.

The increase in NO_x with respect to the oxygen level can be attributed to several reasons. As the oxygen level increases, more free oxygen is available for reacting with nitrogen-containing species to form NO_x . In the meantime, at higher oxygen and steam conditions, more NH_3 is formed (Figs. 7 and 8), and there are two competing effects of NH_3 on NO_x formation. On one hand, NH_3 can react with oxygen to form NO .



The above equation can be regarded as an oxidation reaction of NH_3 , which can be burned as a fuel, resulting in high NO_x emissions [26,27]. On the other hand, NH_3 can be used as a reduction agent to reduce exhaust NO_x emissions, e.g., selective catalytic reduction (SCR) systems in modern diesel engines. These two effects compete with each other and thus the net effect is not linear. Furthermore, the reaction between NH_3 and O_2 is also influenced by the presence of steam. Previous studies show that steam can slow down the reaction of NH_3 and O_2 in forming NO [28]. In the case of seed corn at 40 vol.% oxygen conditions, the moisture level in the syngas is significantly higher than those at other conditions. The high moisture can reduce the conversion of NH_3 to NO , resulting in a slight decrease in NO_x at 40 vol.% oxygen conditions for seed corn (Fig. 9).

5. Conclusions

The effects of oxygen-enriched air and steam gasification on syngas composition are studied experimentally in a pilot-scale, pressurized bubbling fluidized bed reactor. In this study, the oxygen level in the gasifying medium is increased from 21 to 40 vol.% on wet basis while the bed temperature is kept at 800 °C. Three different biomass feedstocks with different nitrogen contents are selected for investigating ammonia formation in syngas at different oxygen levels in the gasifying medium.

The use of oxygen-enriched air reduces the nitrogen dilution effect, thus increasing the syngas heating value. Steam is a source of hydrogen and can result in noticeably higher H_2 and CH_4 in syngas for all feedstocks. In the meantime, steam can also enhance CO production via various mechanisms such as steam reformation and water–gas reactions. On the other hand, steam in high temperature environments can yield OH and H radicals which in turn can react with nitrogen-containing species to form ammonia. Thus, ammonia concentration increases as the steam flow rate increases.

This study demonstrates that oxygen-enriched air and steam mixture is a feasible choice as a gasifying agent and is most effective for the feedstock with low nitrogen and moisture contents. The H_2/CO ratio can also be increased using the present setup. However, the H_2/CO ratio is still moderate and not optimal for synthesis processes to produce liquid fuels. The low H_2/CO ratio is due to a large amount of unreacted steam that remains in the product gas. It is advisable to operate the gasifier at a higher temperature to promote the water–gas shift reaction for more effective conversion of steam to H_2 . Additionally, in order to make syngas more viable and attractive as a renewable energy source, there is a need to explore means of converting ammonia in syngas to molecular nitrogen to prevent excessive NO_x emissions from the subsequent syngas combustion.

Acknowledgement

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